toward the anode was lower and its chromatographic mobility was higher than that of the $\beta$T3 peptide.

For further analysis the abnormal peptide was separated from other peptides by high-voltage paper electrophoresis, first at *p*H 5.4 (*8*) and again at *p*H 1.9 (*9*); it was eluted with 5.7*N* hydrochloric acid and hydrolyzed for 18 hours in a sealed, evacuated tube at 110°C. Then quantitative amino acid analysis of the resultant hydrolysate was made by automated chromatography (*10*). The results appear in Table 1 (*11*).

The amino acid composition of the abnormal peptide indicated that it contained one additional alanyl residue and one less glutamyl residue than did the normal $\beta$T3 peptide, so that one of the two glutamyl residues normally present in the $\beta$T3 section of the $\beta$-chain, at positions $\beta$-22 and $\beta$-26, must have been replaced by alanyl in hemoglobin-G Hsin-Chu. The normal amino acid sequence for $\beta$T3 peptide is

-Val-Asn-Val-Asp-Glu-Val-Gly-Gly-
18 22
Glu-Ala-Leu-Gly-Arg-
26 30

To determine which glutamyl position was affected, analysis by stepwise degradation, by a modified Edman degradation procedure (*12*), was applied to 1-$\mu M$ quantities of the abnormal $\beta$T3 peptide; for comparison, parallel degradation studies were made of the $\beta$T3 peptide from normal hemoglobin-A. Descending paper-chromatographic procedures (*13*) were used for identification of the phenylisothiohydantoin–amino acid derivatives released at each cycle of the degradation. The initial eight sequences in both peptides were determined.

The results were the same in both peptides for the first four positions; in the fifth cycle, glutamic acid was found in the normal $\beta$T3 peptide, whereas alanine was found in the $\beta$T3 peptide from the G-hemoglobin. Three additional cycles were run on both peptides, and the normal amino acid derivatives were obtained. These results were considered sufficient to determine that the anomaly in hemoglobin-G Hsin-Chu involved replacement of a glutamyl residue by one of alanine at position $\beta$-22.

Occurrence of an alanyl residue at position $\beta$-22 is one of the changes characteristic of the $\delta$-chain (*14*). Therefore, as in the earlier study (*2*), it was necessary to determine whether any other $\delta$-like substitutions were present such as those found in the hybrid $\delta$-$\beta$ chains that replace normal $\beta$-chains in the Lepore hemoglobins (*15*). Accordingly the peptides corresponding to $\beta$T2 and $\beta$T5 were isolated by a combination of high-voltage electrophoresis (*8, 9*) and chromatography, hydrolyzed, and analyzed for their amino acid compositions. In both peptides the amino acid distributions were those expected for the $\beta$-chain peptides and not for the $\delta$-chain; the only change found was that described above at the $\beta$-22 position.

The first subject having hemoglobin-G Hsin-Chu had migrated to Taiwan from mainland China; his parents had come from the northern Chinese province of Liaoning. Several other subjects from northern provinces carry similar, electrophoretically slow, hemoglobin variants of which some presumably will prove to be G Hsin-Chu.

Hemoglobin-G Coushatta was found (*2*) in several Alabama-Coushatta Indians now living in eastern Texas. Hemoglobin-G Saskatoon was found (*3*) in several North American Indians of apparently mixed tribal ancestry, now living in Canada, whose recent forebears included Santee Indians who lived in the Dakotas. Final evaluation of the ethnologic significance of the occurrence of this G-hemoglobin, $\alpha_2\beta_2{}^{22\ \mathrm{Glu}\rightarrow\mathrm{Ala}}$, in such widely differing groups as northern Chinese and North American Indians awaits further large-scale studies for more precise determination of the patterns of occurrence and incidences of hemoglobin variants in various ethnic groups.

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## Obsidian Sources Characterized by Neutron-Activation Analysis

Abstract. *Concentrations of elements such as manganese, scandium, lanthanum, rubidium, samarium, barium, and zirconium in obsidian samples from different flows show ranges of 1000 percent or more, whereas the variation in element content in obsidian samples from a single flow appears to be less than 40 percent. Neutron-activation analysis of these elements, as well as of sodium and iron, provides a means of identifying the geologic source of an archeological artifact of obsidian.*

Obsidian artifacts are often recovered from archeological sites considerably removed from geologic sources of the mineral. Occurrence of obsidian on Hopewell sites in the Illinois and Scioto valleys of the eastern United States is only one example; the nearest obsidian flows are in Mexico, New Mexico, and Yellowstone National Park, and on the Pacific Coast. In studies of prehistoric trade patterns, it is desirable to know the true sources.

Recent analysts of prehistoric obsidian artifacts and sources in the Near East (*1, 2*) and the Aegean (*3*) have attempted to demonstrate that each obsidian source may be characterized by elemental analyses. Studies of the elemental content of obsidian have since been extended to New Zealand (*4*) and

North America (*5, 6*) in order to relate artifacts to their sources.

Our interest in this problem was twofold: in developing methods of analysis of obsidian and other geologic samples to enable examination of thousands of geologic and archeological samples a year, and in determining the geochemistry of obsidian. In order to identify obsidian with a particular geologic source, one must assume that the composition is uniform throughout a single flow but is distinguishable from that of other obsidian flows. No formal test of the first part of this assumption has been reported.

In order to test this hypothesis, more than 1000 samples of obsidian from single natural flows, in distinct volcanic regions, were examined by neutron-activation analysis (*2, 7*).

The specimens and chemical standards are irradiated for 40 seconds with thermal neutrons, and the induced $^{24}$Na and $^{56}$Mn activities are determined. During the period of 2 to 24 hours following the irradiation, more than 99 percent of the observed activity is due to only these two nuclides; the remainder is due mainly to $^{42}$K and very small amounts of $^{140}$La, $^{31}$Si, and $^{46}$Sc. Less than 1 percent of the $^{56}$Mn activity produced in the obsidian is due to $^{56}$Fe(*n,p*) activation as determined by analysis of separate samples of iron compounds irradiated with the obsidian. The Na and Mn isotopes are analyzed with a NaI(Tl) detector (5- by 5-cm well) coupled to a single-channel analyzer (model-530 spectrometer; Baird Atomic Co.). Because the Mn content of obsidian is so low, some of the $^{24}$Na activity must be suppressed: the energy "window" of the analyzer is centered on the 0.845-Mev gamma-ray peak of $^{56}$Mn, and only the energy range from 0.76 to 0.93 Mev is included.

The entire procedure is automated, and 100 obsidian samples and standards are analyzed together. The activity is measured over a period of 22 hours. A computerized method of least squares resolves the decay data into its $^{24}$Na and $^{56}$Mn components. Since the $^{24}$Na and $^{56}$Mn half-lives are only 15 and 2.6 hours, respectively, the activity is almost completely dissipated within 1 week, and the irradiations and analyses can be repeated for replicate sets of data. Typically the standard deviations of the mean for the replicate Na and Mn assays are within about 5 percent of the mean.

This decay-curve method of analysis is checked with gamma-ray pulse-height

Table 1. Elemental contents of various samples of obsidian.

| Na (%) | | | Mn (× $10^2$%) | | | La (× $10^2$%) | | | Fe (%) | | | Rb (× $10^2$%) | | | Sc (× $10^4$%) | | | Sm (× $10^3$%) | | | Na : Mn | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *N* | Av. | Range | *N* | Av. | Range | *N* | Av. | Range | *N* | Av. | Range | *N* | Av. | Range | *N* | Av. | Range | *N* | Av. | Range | *N* | Av. | Range |
| *Obsidian Cliff Y-samples* | | | | | | | | | | | | | | | | | | | | | | | |
| 23 | 3.3 | 3.0–3.6 | 23 | 2.2 | 2.0– 2.4 | 12 | 0.99 | 0.92–1.2 | 12 | 1.1 | 0.96–1.3 | 12 | 1.9 | 1.7–2.3 | 12 | 1.5 | 1.3–1.8 | 12 | 1.7 | 1.4 –1.9 | 23 | 151 | 141–162 |
| *Obsidian Cliff random samples* | | | | | | | | | | | | | | | | | | | | | | | |
| 50 | 3.3 | 2.9–3.6 | 50 | 2.1 | 1.9– 2.6 | 11 | 1.1 | 0.93–1.2 | 11 | 1.1 | 1.0 –1.3 | 11 | 2.1 | 1.8–2.4 | 11 | 1.6 | 1.3–1.8 | 11 | 1.6 | 1.4 –1.9 | 50 | 155 | 132–171 |
| *Cerro de las Navajas* | | | | | | | | | | | | | | | | | | | | | | | |
| 67 | 4.4 | 3.9–4.8 | 67 | 11.8 | 10.1–13.4 | 10 | 0.72 | 0.64–0.81 | 9 | 1.9 | 1.7 –2.1 | 9 | 1.7 | 1.4–1.9 | 9 | 4.3 | 3.8–5.0 | 10 | 1.2 | 1.0 –1.4 | 67 | 37 | 33– 44 |
| *Glass Mountain* | | | | | | | | | | | | | | | | | | | | | | | |
| 11 | 3.6 | 3.4–4.0 | 11 | 3.3 | 3.0– 3.8 | 11 | 0.41 | 0.37–0.49 | 11 | 1.7 | 1.5 –1.8 | 11 | 1.2 | 1.0–1.4 | 11 | 5.9 | 5.3–6.4 | 11 | 0.75 | 0.64–0.80 | 11 | 112 | 107–118 |
| *Napa Valley, California* | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | 3.7 | 3.4–4.1 | 3 | 1.7 | 1.6– 2.0 | 3 | 0.57 | 0.55–0.60 | 3 | 1.0 | 0.90–1.2 | 3 | 1.4 | 1.3–1.7 | 3 | 3.5 | 3.2–4.2 | 3 | 1.1 | 1.1 –1.1 | 3 | 212 | 206–212 |
| *Mono Lake, California* | | | | | | | | | | | | | | | | | | | | | | | |
| 18 | 3.4 | 3.0–3.9 | 18 | 3.7 | 3.4– 4.3 | 6 | 0.42 | 0.38–0.55 | 6 | 1.0 | 0.91–1.1 | 6 | 1.4 | 1.1–1.5 | 6 | 2.5 | 2.1–2.7 | 5 | 0.83 | 0.69–0.89 | 18 | 91 | 83– 97 |
| *Cougar Mountain, California* | | | | | | | | | | | | | | | | | | | | | | | |
| 15 | 3.5 | 2.9–4.0 | 15 | 3.4 | 2.8– 4.0 | 4 | 0.33 | 0.27–0.38 | 4 | 1.1 | 0.98–1.2 | 4 | 1.2 | 1.0–1.4 | 4 | 5.0 | 4.6–5.5 | 4 | 1.1 | 0.90–1.3 | 15 | 100 | 89–108 |
| *Observed ranges of means for 60 tested flows* | | | | | | | | | | | | | | | | | | | | | | | |
| | | 2.0–6.0 | | | 1.7–25.0 | | | 0.3–3.5 | | | 0.6–3.3 | | | 0.5–5.1 | | | 0.4–12.8 | | | 0.4–4.5 | | | 30–212 |

Table 2. Elemental contents of samples of obsidian from Glass Mountain. USGS, U.S. Geological Survey.

| USGS No. | Na (%) | Mn ($\times 10^2$%) | La ($\times 10^2$%) | Fe (%) | Rb ($\times 10^2$%) | Sc ($\times 10^4$%) | Sm ($\times 10^3$%) | Na : Mn |
|---|---|---|---|---|---|---|---|---|
| 3171-5A | 3.47 | 3.24 | 0.43 | 1.8 | 1.2 | 6.1 | 0.80 | 107 |
| 3171-6A | 3.91 | 3.53 | .43 | 1.8 | 1.2 | 6.4 | .80 | 111 |
| 3171-7A | 3.58 | 3.13 | .37 | 1.7 | 1.1 | 5.4 | .69 | 114 |
| 3171-3A | 3.63 | 3.22 | .39 | 1.8 | 1.1 | 6.1 | .78 | 113 |
| 3171-3A | 3.65 | 3.26 | .40 | 1.5 | 1.0 | 5.1 | .76 | 112 |
| 3172-1A | 3.62 | 3.35 | .37 | 1.6 | 1.1 | 5.4 | .68 | 108 |
| 3172-2A | 3.53 | 3.03 | .41 | 1.8 | 1.2 | 6.4 | .82 | 116 |
| 3172-2C | 3.41 | 2.92 | .40 | 1.7 | 1.2 | 5.9 | .73 | 117 |
| 3172-3A | 3.94 | 3.84 | .42 | 1.8 | 1.3 | 6.2 | .79 | 103 |
| 3173-6B | 3.66 | 3.30 | .49 | 1.8 | 1.4 | 6.2 | .78 | 111 |
| 3175-3D | 3.51 | 2.96 | .38 | 1.6 | 1.0 | 5.3 | .64 | 118 |

spectra of selected samples (and standards): the Na and Mn contents calculated by use of these data agreed with the average values obtained by the sample-changer decay-curve method.

Samples representing both the means and minimum-maximum ranges of the Na and Mn contents, together with chemical standards, are then irradiated with neutrons in a reactor for 24 hours. Besides $^{24}$Na and $^{56}$Mn, detectable amounts of the longer-lived radioisotopes $^{140}$La, $^{59}$Fe, $^{46}$Sc, $^{86}$Rb, and $^{153}$Sm, as well as about ten other species, also are produced. Analysis for these elements is performed by pulse-height gamma-ray spectrometry with a Ge(Li) detector; this analysis is not repeated, and the data are valid within about 20 percent.

The Y-samples (Table 1) are specimens from a small (5 by 5 by 2.5 cm) block of obsidian from Obsidian Cliff, Yellowstone National Park; the random samples from Obsidian Cliff were taken almost at random from across the obsidian flow (*8*). The third set of specimens (Table 1) are from five different "obsidian mines" on a single flow in the Cerro de las Navajas, Hidalgo, Mexico (*9*). The fourth set, from Glass Mountain, California, are wholly random from various points on the flow (*10*).

In all instances (Table 1) the computed means for the seven elements and the Na : Mn ratios for the Obsidian Cliff Y-samples and random specimens compare favorably: the variation in Mn is slightly larger for the random samples, but for all elements this range is typically 30 to 40 percent. Thus these data suggest that the Y-samples are representative of the mean contents and ranges of variation to be expected across the entire flow.

The Cerro de las Navajas specimens, however, differ significantly from those from Obsidian Cliff in Na, Mn, La, Fe, and Sc contents and in Na : Mn ratio; again the minimum-maximum range is less than 40 percent. By elemental analysis these Cerro de las Navajas mines are indistinguishable from each other.

The spreads in the data for individual specimens from Glass Mountain (Table 2) also are less than 40 percent; the elements appear to be uniformly distributed throughout the flow. There are no series of element clusters within the flow itself. These samples are easily distinguished from those from Obsidian Cliff by their Mn, La, Fe, Sc, and Sm contents and by their Na : Mn ratios. Contents of Mn, Sc, and Sm and Na : Mn ratios differentiate the Glass Mountain and Cerro de las Navajas specimens.

This type of analysis is applicable to smaller geographic regions and single volcanic areas (*1–5*). Table 1 compares three other California flows of obsidian with Glass Mountain. The Napa Valley specimens are extremely low in Mn but have the highest Na : Mn ratio found by our worldwide survey. Napa Valley differs from Glass Mountain in Fe content also, from Cougar Mountain in Sc and La contents, and from Mono Lake in Sc content.

The Sc content of Mono Lake obsidian is sufficiently different to distinguish this flow from the Glass Mountain and Cougar Mountain flows; its Fe content also is lower than that of Glass Mountain. Cougar Mountain and Glass Mountain may be separated on the basis of Fe and Sm contents. Parks and Tieh (*5*) have shown that the Glass Mountain and Mono Lake flows are characterized by their Sr : Rb ratios also.

Thus the assumption that chemical composition is uniform within a single obsidian flow seems to be warranted, so that samples from any one section may be taken to represent the entire flow. Flows vary sufficiently to allow characterization by element contents. The 40-percent internal variation may be taken as a general guide to the amount of variation to be expected when flows are studied by activation analysis; it is considerably less than the variation (frequently 100 percent) shown by optical spectrography (*1*).

We believe that much of the variation encountered in the activation analyses is really statistical, and that the true variation is somewhat less (*7*). With this variation in mind one should note, from the final column in Table 1, that Mn, La, Sm, and Sc appear to be ideal elements for characterizing obsidians; they show a mean minimum-maximum variation, for the 60 flows, of more than ten times (1000 percent). The same range of variation has been determined for Ba and Zr in obsidian flows in the Near East (*1*). Neutron-activation analysis of obsidian provides for the archeologist a method for matching his obsidian artifacts with their sources and so determining prehistoric trade routes.

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